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STUDIES ON LOW-TEMPERATURE LIGNITE TAR
II. CHARACTERIZATION OF MATERIALS OTHER THAN TAR ACIDS

by

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As described in the first paper of this series, primary tar from the low-temperature carbonization of lignite can be processed in a number of different ways. The various products obtainable contain a wide assortment of chemicals and classes of chemicals in different combinations. The purpose of this paper is to describe what has been learned about the different classes of chemicals in primary tar. The major effort was directed toward identifying the classes of the chemicals rather than searching out the identities and quantities of individual components. However, some individual compounds were studied in the process.

The most important single characteristic of low-temperature tar is that usually, for each class of compounds found, all the homologues are present. However, no one compound is present in a large amount. In the primary tar, as received, phenol is the most abundant single compound, in about one per cent.

Primary Tar

Primary tar is composed of materials that distill at temperatures from below 100 C to about 350 C, as well as high-molecular-weight, pitch-like materials. All characterization work has been done on distillates. However, it is believed that the residual material probably has the same general proportions of chemical compound classes as do the distillable fractions.

Primary tar is composed of tar acids, tar bases, and neutral oil as determined by their relative solubility or insolubility in caustic or dilute acid. The solvent-extraction process described in Paper I of this series divides the primary tar so that most of the tar acids are soluble in the

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methanol-water phase, and most of the neutral oil is soluble in the hexane phase; the tar bases are divided quite evenly between the two phases.

Figure 1 shows the boiling point, refractive index, and density curves obtained from a vacuum fractional distillation of a vacuum-flash distillate of a primary tar studied early in the program. The individual fractions were composited to fifteen fractions. All of these, except for the lowest boiling composites, contained about the same proportions of tar acids, tar bases, and neutral oil. The fall in refractive index and corresponding rise in density has not been explained or studied. These effects might have resulted from azeotrope formation because neither tar acids nor neutral oil showed this effect when they were distilled separately. The average composition of distillates of lignite tar is as follows:

Tar acids	25 – 30 per cent
Tar bases	4 – 5 per cent
Neutral oil	65 – 70 per cent

The remainder of this paper and subsequent papers in the series describe what was learned when these three classes of tar constituents were studied individually.

Tar Acids

Tar acids, or those materials soluble in caustic, were found to be primarily phenolic compounds with no more than two per cent of aliphatic carboxylic acids. For this work, tar acids were divided into two parts: low-boiling tar acids and high-boiling tar acids. The dividing atmospheric boiling point was 235 C, as this temperature is slightly higher than the 225 C boiling point of the least volatile xylenol (3,4), and thus insures the inclusion of all the xylenols in the low-boiling tar acids. The separation was generally made by distilling off the low-boiling tar acids under vacuum in a nitrogen atmosphere. The high-boiling tar acids were sometimes distilled at temperatures up to those equivalent to 300 to 350 C at atmospheric pressure. In such cases, only about 50 to 60 per cent of the high-boiling tar acid fraction distilled.

The composition of the low-boiling tar acids was studied by infrared analysis after the acids had been converted to their methyl ethers. This work is described in detail in Paper III of this series. Phenol was found to be the most abundant single tar acid. All of the cresols, xylenols, and ethylphenols were also present in low-boiling tar acids.

The high-boiling tar acids distilling up to 335 C were also studied. This work is described in detail in Paper IV of this series. Alkylated phenols, naphthols, indanols, and polyhydroxylic phenols were the predominant classes of compounds found in high-boiling tar acids.

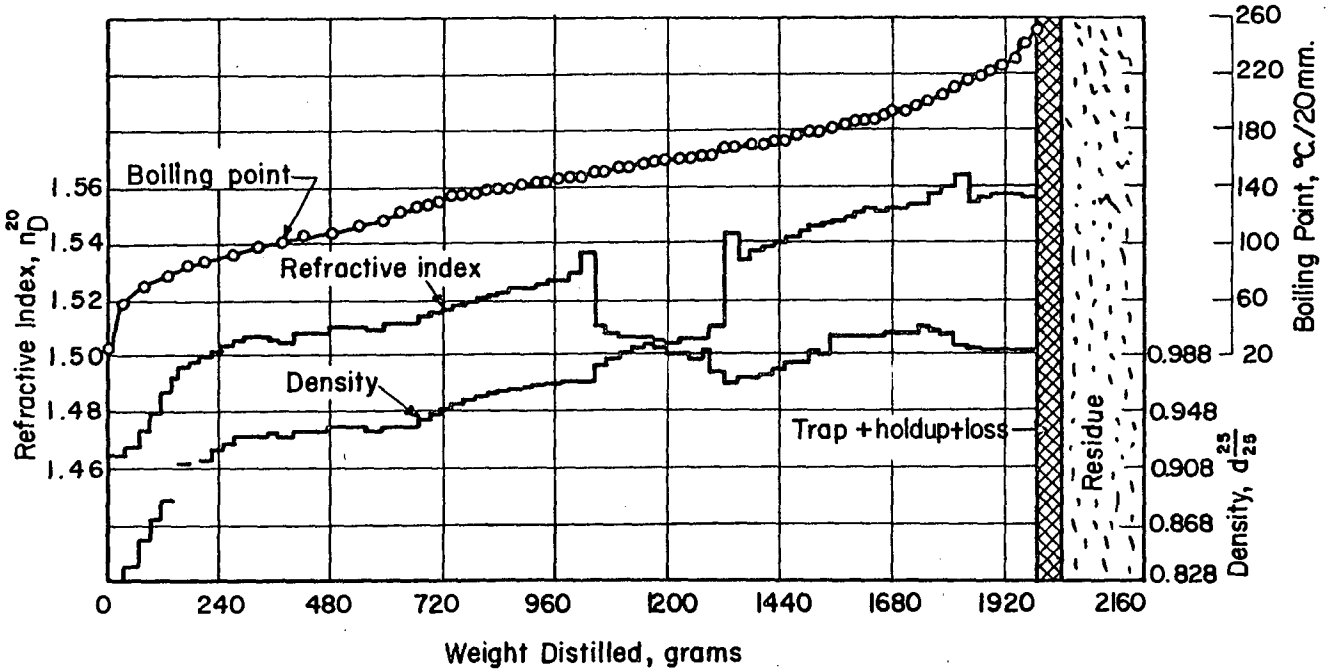


FIGURE I. FRACTIONATION BY DISTILLATION OF VACUUM-FLASH DISTILLATE

Tar Bases

Tar bases, or those materials soluble in dilute mineral acid, are present in tar distillates to the extent of only 3.5 to 4.5 per cent. As they represent only a small part of the tar, only limited studies were made of their nature. Actually, all of the tar bases cannot be easily recovered, and yields of less than 1.5 per cent were realized by conventional recovery methods. Distillations, spot tests, and paper chromotography indicated that tar bases are primarily nitrogen heterocyclics of the pyridine and quinoline types. No evidence was obtained of aniline derivatives.

Neutral Oil

Neutral oil, which represents more than two-thirds of primary tar, is composed primarily of hydrocarbons. These hydrocarbons are paraffins, olefins, and aromatics. Also present are nonacidic "polar compounds" which contain oxygen, sulfur, or nitrogen. Figure 2 shows the results of fractionating neutral oil in a Podbielniak Hypercal distillation unit. Evidence of some degree of separation is shown by the plateauing in the boiling-point curve and the periodic rise and fall of the refractive index curve. Infrared studies of selected fractions showed those corresponding to the maxima of the refractive index curve to be predominantly aromatic, and those corresponding to the minima to be predominantly aliphatic. The periodicity is evidence for the homologous nature of the chemicals in primary tar.

Silica-gel-displacement chromotography was used to assay neutral oil for content of paraffins, olefins, and aromatics. Figure 3 shows a typical curve obtained by the method of Dinneen, et al.[1,2]*. These results are compared in Table 1 with those obtained by a conventional sulfuric acid extraction method as described by Reynolds and Holmes.[3] There is no satisfactory explanation for the remarkable differences in the paraffin and aromatic values obtained by the two methods. However, the polar compounds, which are believed to be present in about 20 per cent, could be the source of difference. They are classed as "aromatics" by the silica gel method, and as olefins in the sulfuric acid method.

The various classes of compounds in neutral oil have been separated and studied for the types of structures present. Infrared spectroscopy has been the chief analytical technique used for identification of structural features.

*References are located at the end of this report.

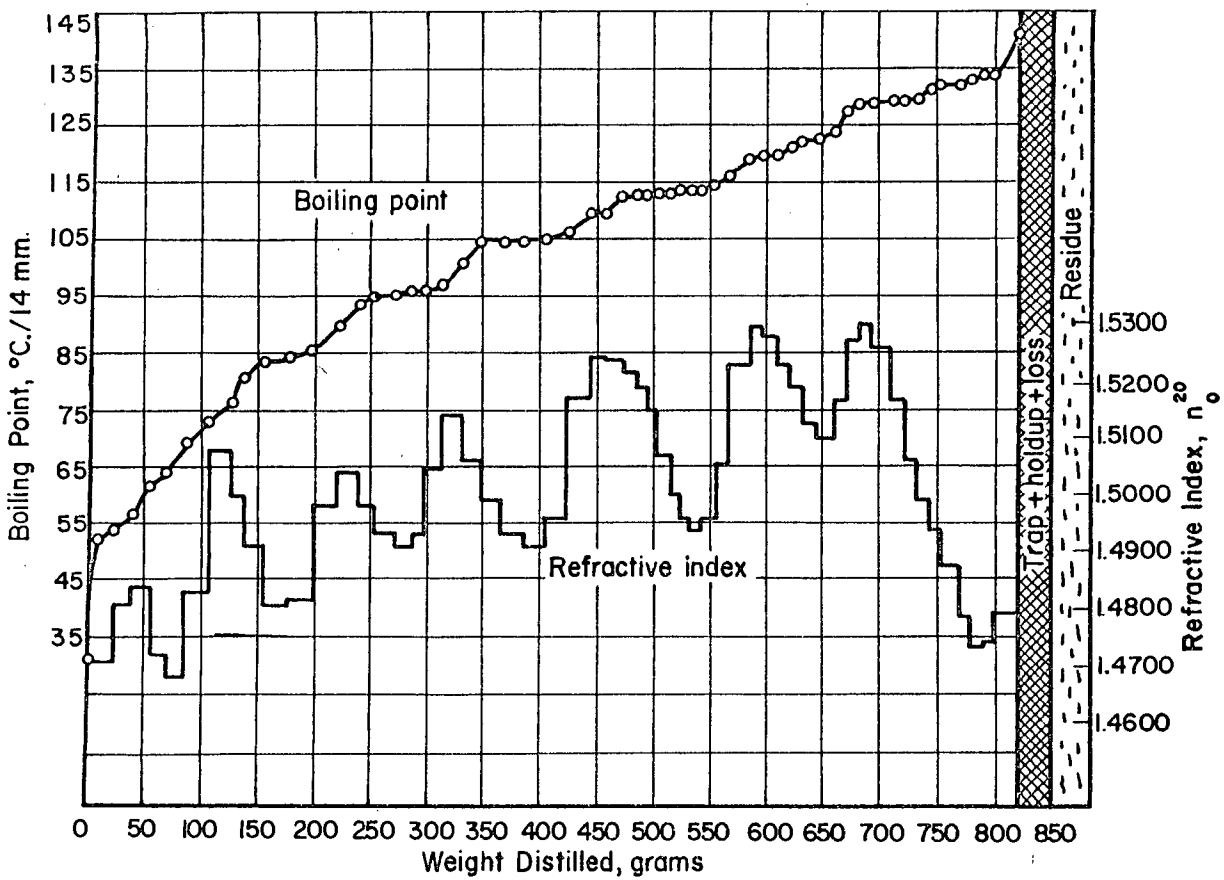


FIGURE 2. PRECISION FRACTIONATION OF NEUTRAL OILS

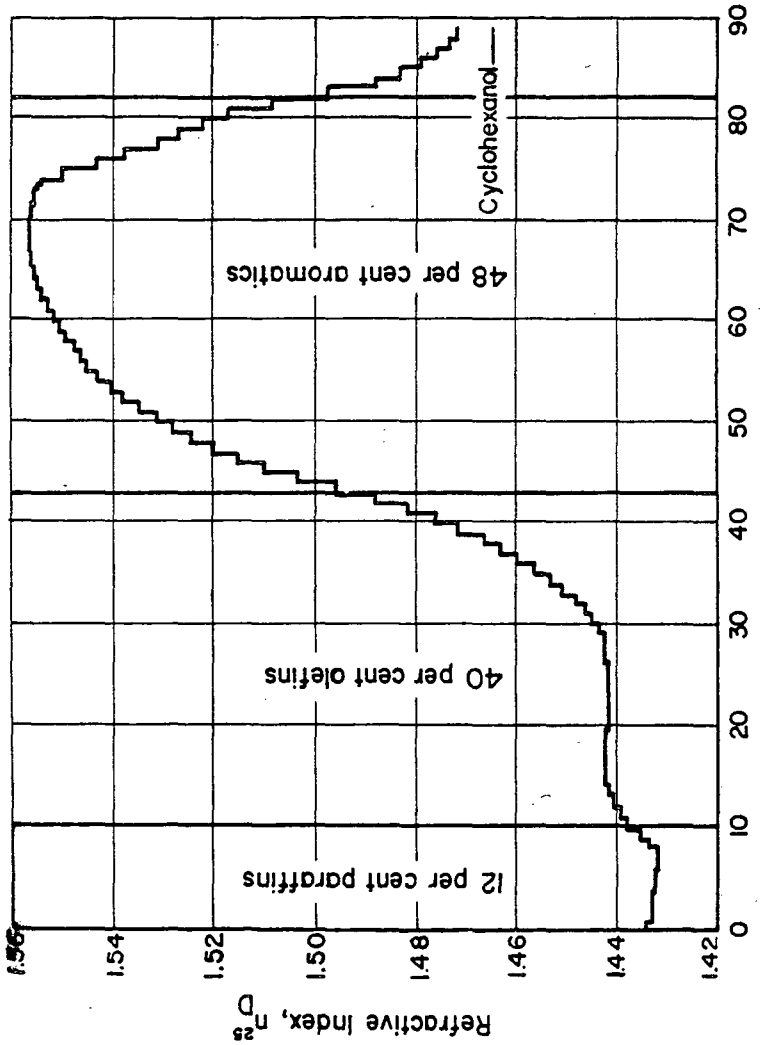


FIGURE 3. SILICA-GEL ADSORPTOGRAM FOR 35 PER CENT NEUTRAL OIL

TABLE 1. COMPOSITION OF NEUTRAL OIL

Component	Method of Analysis	
	H_2SO_4	Si Gel
Paraffins	33	11-13
Olefins	43	35-40
Aromatics	24	48-53

Paraffins

The paraffins in lignite tar are primarily straight-chain hydrocarbons with a small amount of branching. The location of the branching in the paraffins is not known, but it is probably random. About one-third of the paraffins form an adduct with urea. This indicates that the adducted paraffins are either unbranched or that the branching is close to the end of the hydrocarbon chain. Hydrocarbon ring analysis based on physical properties showed that the paraffins and olefins combined contain about 20 per cent ring carbon atoms.

Paraffins were isolated from high-boiling fractions of neutral oil as colorless waxes. Although considerable efforts were made to purify these waxes to yield high-melting solids, the highest melting-point range attained was 40 to 47 C. Infrared and elemental analyses of these waxes showed them to contain only carbon and hydrogen.

Olefins

Early infrared studies on selected olefin fractions, separated from neutral oil by silica gel, showed the three major kinds of olefins present to be terminal or alpha, trans-internal, and tertiary.

To learn more about the olefins, a study was made of the effect of various strengths of H_2SO_4 on the removal of olefins. Figure 4 shows how the percentage of neutral oil extracted rises as stronger H_2SO_4 is used, a sharp rise taking place at 70 per cent acid. At this acid strength, the bromine number begins to drop rapidly. The material extracted by the more dilute acids is believed to be mostly polar compounds (discussed in a later section). Figure 5 shows a silica-gel curve of neutral oil washed with cold 78 per cent H_2SO_4. The proportion of olefins remaining was slightly higher than in the original neutral oil. Table 2 shows the calculated amounts and the proportions of the paraffins, olefins, and aromatics that were extracted by the acid.

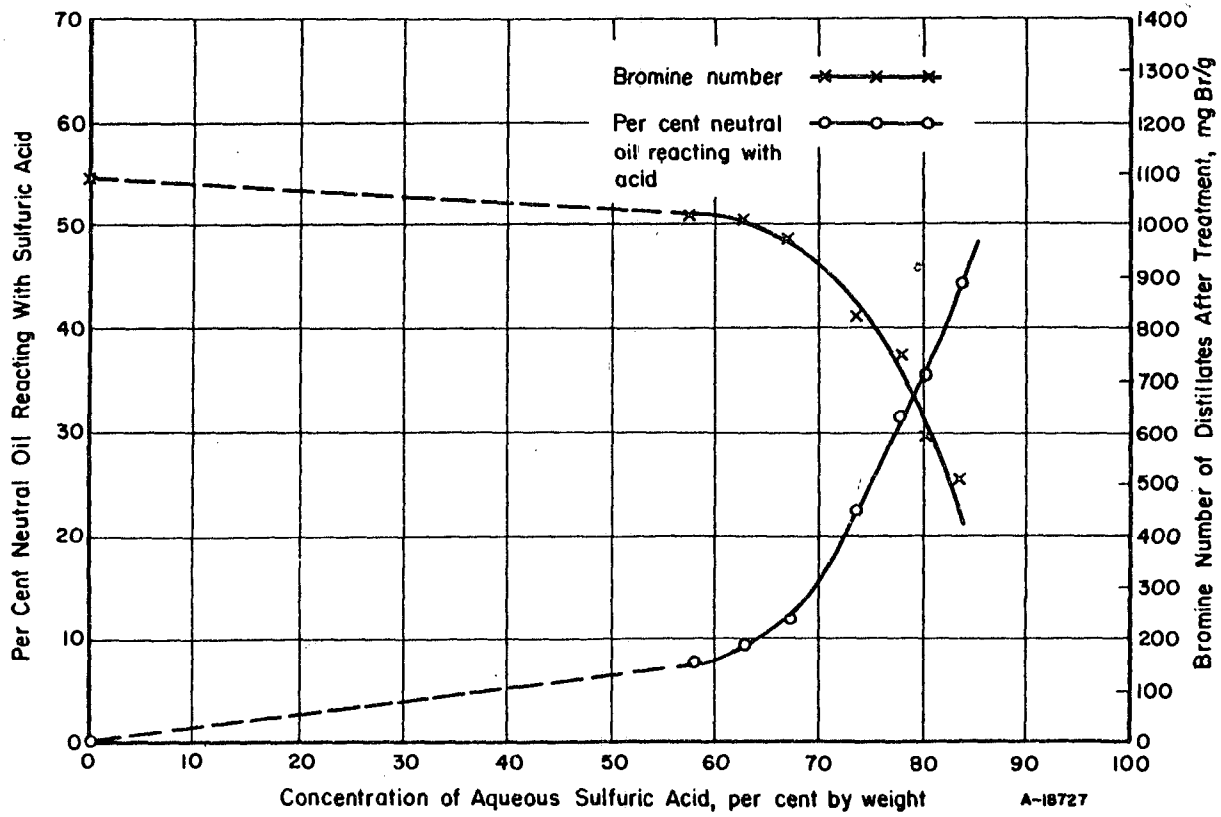


FIGURE 4. EFFECT OF VARIOUS STRENGTHS OF SULFURIC ACID ON NEUTRAL OIL

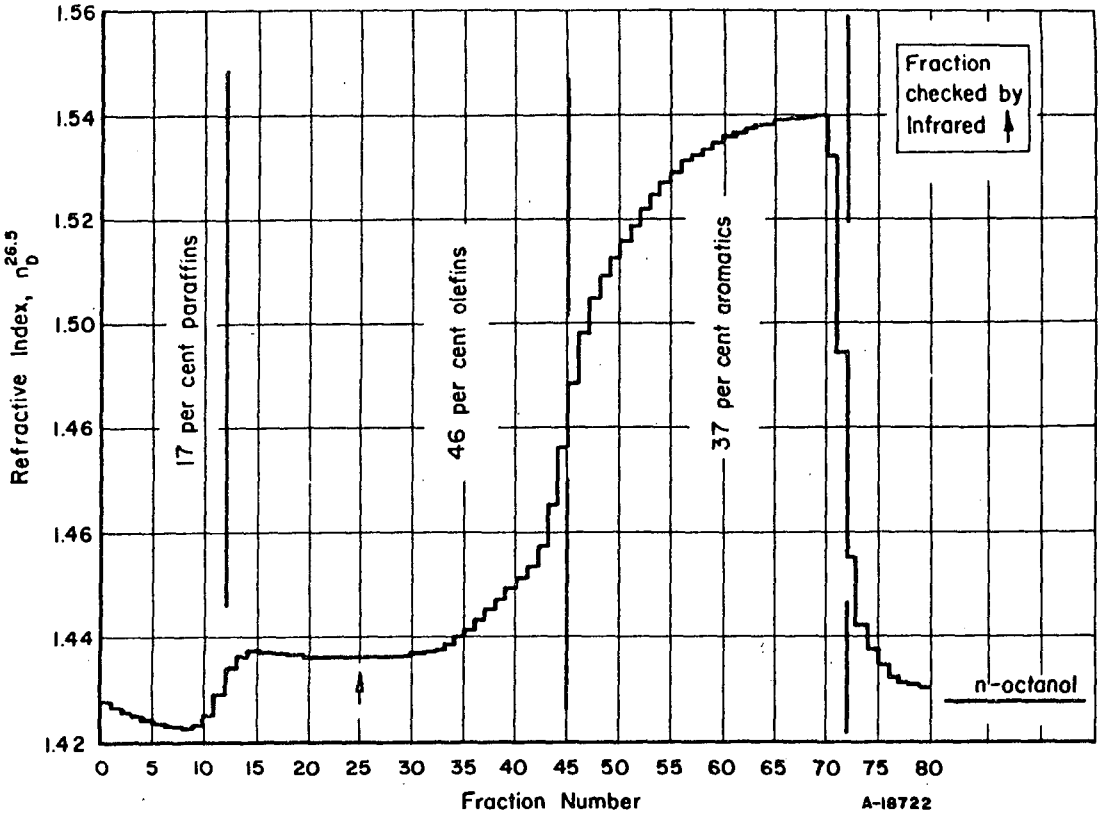


FIGURE 5. SILICA-GEL ADSORPTOGRAM FOR NEUTRAL OIL WASHED WITH COLD 78 PER CENT SULFURIC ACID

TABLE 2. COMPOSITIONS OF NEUTRAL OIL BEFORE AND AFTER BEING WASHED WITH COLD 78 PER CENT H_2SO_4

	Neutral Oil Components[a], per cent			
	Paraffins	Olefins	Aromatics	Total
Original neutral oil	12	40	48	100
Washed neutral oil	11.6	31.3	25.2	68.1
Amount removed	0.4	8.7	22.8	31.9
Percentage of composition removed material	1+	27+	71+	--

(a) Determined by displacement silica gel chromotography.

About one-half of the olefins present in lignite tar are α-olefins. Because the double bond is located at the end of the molecule, α-olefins can form adducts with urea providing the remainder of the chain is not branched. This urea reaction, together with the selective separation of paraffins and olefins on silica gel, provided a means of obtaining enriched samples of α-olefins. Figure 6 shows how α-olefins were separated from a 200 to 300 C cut of hexane solubles obtained from the solvent extraction process. The laboratory separation described yielded a water-white olefin fraction which was about 75 per cent α-olefin. Some trans- and tertiary-olefins were also present.

The individual small fractions obtained from the silica-gel separation of the olefins from the whole adducted oil were subjected to further study. Table 3 shows the information gained about average molecular weight, ratio of α-olefins to total olefins, and total double bonds per molecule as determined by infrared and by bromine number. The average length of the olefin chains ranged from 14 to 16 carbon atoms, with most of the fractions containing about one double bond per molecule. Earlier olefin fractions contained somewhat less unsaturation, which was probably evidence of incomplete separation of paraffins from the olefins. Later olefin fractions contained somewhat more unsaturation which could be evidence of multiple unsaturation, although no infrared evidence was found of conjugated unsaturation. As these olefins had adducted with urea, this might be interpreted to suggest the presence of diolefins in which both double bonds are located terminally.

No work was done to prove the presence or absence of cyclic olefins in neutral oil, although such compounds are expected to be present. A ring analysis was made of the combined paraffin-olefin fraction, as separated by silica gel, of a 200 to 300 C cut. Various physical measurements were used as recommended by Deanesley and Carleton[4] to calculate the results, which

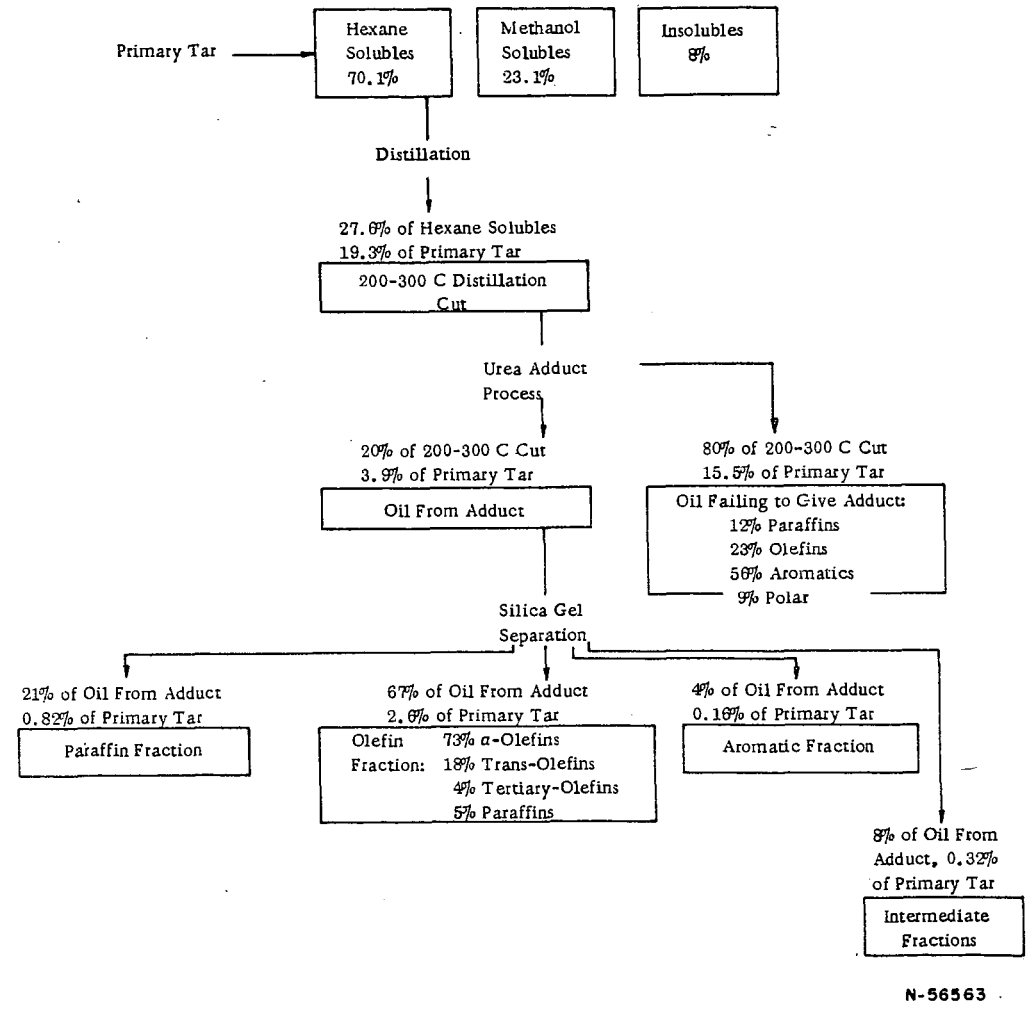


FIGURE 6. SEPARATION OF A 200-300 C BOILING CONCENTRATE OF α-OLEFINS FROM PRIMARY TAR

indicated about one-fourth of the carbon atoms were naphthenic. This same fraction was found by infrared to contain 61 per cent olefins.

TABLE 3. CHARACTERIZATION OF SILICA-GEL CHROMATOGRAPHY CUTS OF OIL FROM UREA ADDUCT OF DISTILLATE OF HEXANE SOLUBLES

Fraction	Refractive Index, n_D^{20}	Comments[a]	Molecular[b] Weight	Ratio of $RCH{=}CH_2$ (Alpha) Olefins to Total Olefins[c]	Total Double Bonds/Mol by Infrared	Total Double Bonds/Mol by Bromination[d]
1	1.4344					
2	1.4336					
3	1.4328	Paraffins				0.0
4	1.4322					
5	1.4317					
6	1.4337	Intermediate				
7	1.4385		233	0.74	0.6	
8	1.4389					0.7
9	1.4387					
10	1.4386		225	0.78	0.8	
11	1.4386					0.8
12	1.4388					
13	1.4387		215	0.77	0.9	
14	1.4390	Olefins				0.9
15	1.4392	67 Per Cent				
16	1.4393		209	0.77	1.0	
17	1.4396					1.0
18	1.4397					
19	1.4399		206	0.77	1.0	
20	1.4401					1.1
21	1.4412			0.75	1.1	1.2
22	1.4458		198	0.75	1.3	
23	1.4604	Intermediate				
24	1.4855	Aromatics				
25	1.4382	n-Octanol				
26	1.4330					

(a) Based on n_D^{20} and infrared spectroscopy.

(b) Determined cryoscopically in benzene.

(c) Determined by infrared spectroscopy. The olefins other than α-olefins remained about 75 per cent trans ($RC(H){=}C(H)R$) and 25 per cent tertiary ($R_1R_2C{=}CH_2$) from fraction to fraction.

(d) Br-BrO_3 method, ASTM D1158-55T (1955). Values under 1 probably indicate paraffin contamination whereas values over 1 may indicate a small amount of multiple unsaturation.

Aromatics

A concentrate of aromatics was obtained from neutral oil by the use of butyrolactone as selective solvent. The aromatic fraction was further purified by the use of silica gel and sodium amide in attempts to remove nonaromatics and particularly the polar compounds. The material was

carefully rectified at reduced pressures into 45 fractions over a calculated atmospheric boiling point range of 140 to 290 C. Table 4 summarizes the types of hydrocarbons definitely identified by infrared analysis of the individual fractions. Polar compounds were evident in the higher boiling fractions. Benzofuran and 2-methylbenzofuran were tentatively identified as major nonhydrocarbon contaminants.

TABLE 4. SUMMARY OF HYDROCARBON TYPES FOUND BY INFRARED SPECTROSCOPY IN FRACTIONS OF REFINED AROMATIC CONCENTRATE

Boiling Range, C/1 atmos.	Characterization
140-163.0	Principally xylenes
157.1-181.5	C_9 aromatics, principally trimethyl benzenes
175.5-205.0	C_9 and higher aromatics including indene and hydrindene
202.0-230.5	Naphthalene plus other aromatics
222.5-251.5	Methyl naphthalenes
247.5-290.5	Possibly dimethyl naphthalenes plus other aromatics

Ring analysis of the aromatic concentrate based on physical properties showed the average structure to correspond to methyl- or ethyltetralin. However, this figure may be in error because of polar contaminants. There was little evidence of any significant amount of polynuclear aromatics or long-chain alkylaromatics. Even though special efforts had been made to remove nonhydrocarbon contaminants, elemental analysis showed the concentrate to contain sulfur, nitrogen, and oxygen (by difference). If the nonhydrocarbon material had the same average molecular weight as the aromatics with one hetero atom per molecule, the various contaminants would be present as follow:

Hetero Atom	Elemental Percentage in Concentrate	Calculated Contaminant Percentage
S	2.4	12.1
N	0.2	2.5
O	1.6	16.1

These figures total 30 per cent and may be high, as oxygen was figured by difference.

Polar Compounds

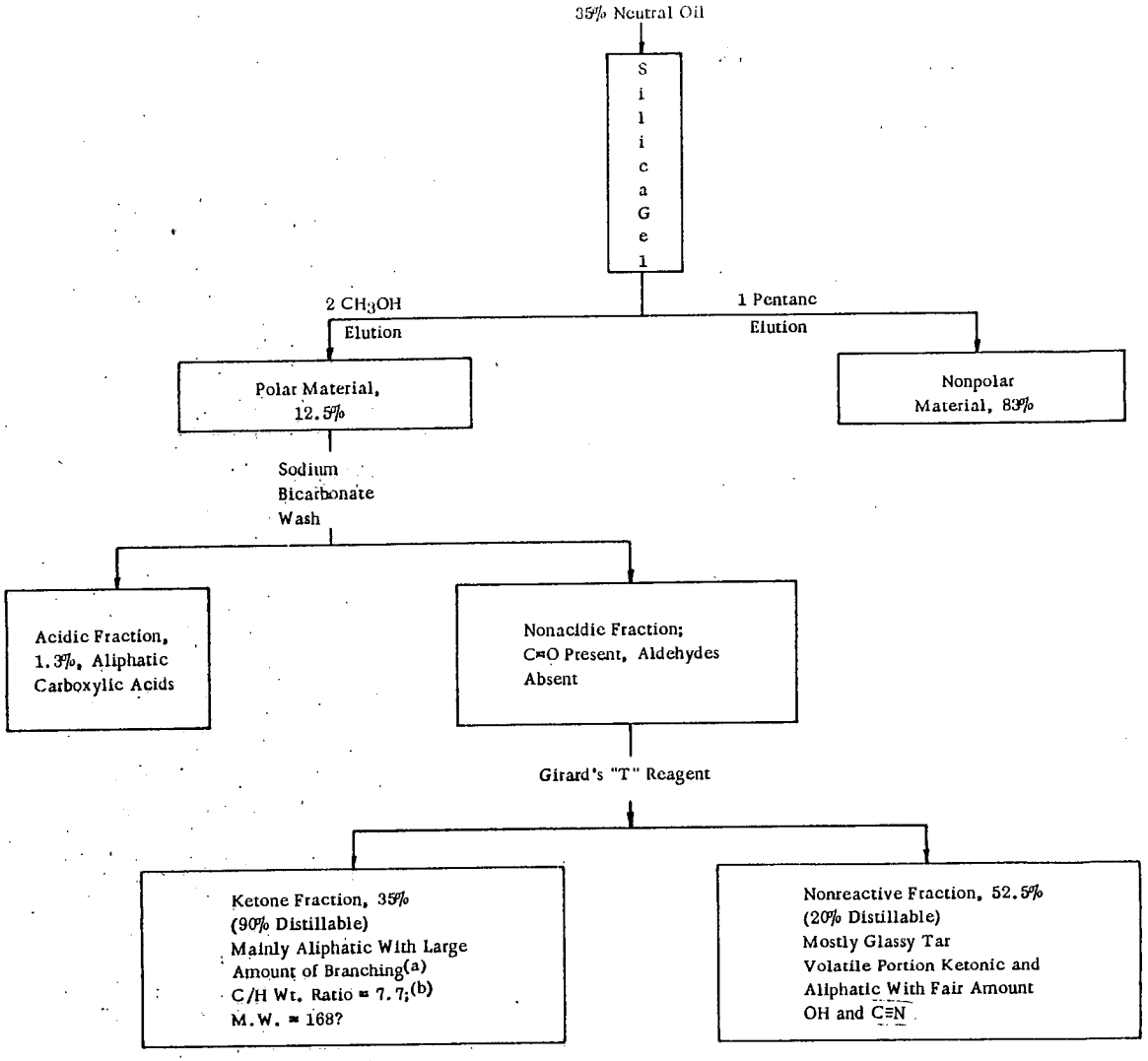
A number of separation methods were applied to neutral oil in attempts to obtain polar compounds free of hydrocarbons. The only method that was reasonably successful involved use of silica gel and elution chromotography as shown in Figure 7. Although other information suggests that neutral oil contains about 20 per cent of polar compounds, only 12.5 per cent was isolated by this particular method.

Infrared indicated that imino, hydroxyl, and cyano groups were present in these polar compounds. However, the major chemical class was ketones. Further concentration and study of the ketones showed the distillable ketones to be primarily aliphatic with a large amount of branching. It will be shown in Paper IV that ketones are the principal contaminant in tar acids.

Sulfur-containing compounds are also present in polar compounds, but spectral evidence is not satisfactory for identification of most classes of sulfur compounds. Furthermore, although chromatography is often effective for the separation of sulfur compounds from hydrocarbons, the sulfur compounds in lignite tar could not be cleanly separated by this technique. It has been found that the sulfur compounds in lignite tar are chemically quite unreactive. Reactive compounds such as thiols and disulfides appear to be present, but in relatively low concentration as compared with aliphatic and cyclic sulfides. Thiophenes were not present; since they are relatively strong infrared absorbers, any significant amounts would have been detected.

Summary

Chemically, primary tar is composed of about 26 per cent tar acids, 4 per cent tar bases, and 70 per cent neutral oil. The make-up of Texas lignite tar by classes of chemicals is summarized in Table 5. Considerably more effort will be needed to obtain more detailed data. This is particularly true for the constituents in the high-boiling fractions of the tar. In any one of the classes of chemicals, a large number of individual chemical compounds are present.



(a) Iodoform test negative.
(b) The C/H ratio of an aliphatic ketone in this range is about 6.0 whereas benzophenone has a C/H ratio of 15.6

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FIGURE 7. STUDY OF POLAR MATERIAL IN 35 PER CENT NEUTRAL OIL

TABLE 5. SUMMARY OF CHEMICAL CLASSES IN TEXAS LIGNITE TAR

Tar acids 26%	
	Low-boiling - 5% - phenols, cresols, xylenols, ethylphenols
	High-boiling - 21% - phenols, naphthols, indanols, polyhydroxylic phenols
Neutral oil 70%	
	Paraffins - 10% - straight chain, lightly branched
	Olefins - 25% - alpha, trans-internal, tertiary
	Aromatics - 21% - benzenes, naphthalenes, hydrindenes, indenes
	Polar compounds - 14% - ketones, sulfides, nitriles
Tar bases 4%	
	Heterocyclics - 4% - pyridines, quinolines

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